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# Project Summary

# A Cryogenic Preconcentration—Direct FID (PDFID) Method for Measurement of NMOC in Ambient Air

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ORIGINAL

**Accurate measurements of atmospheric concentrations of nonmethane organic compounds (NMOC) are necessary in the application of photochemical models that are used by states in developing the control strategies needed to achieve compliance with ambient air quality standards for ozone. NMOC measurements obtained with available continuous NMOC analyzers have often been of inadequate quality. Speciated gas chromatographic measurements, though adequate, are excessively difficult and expensive where speciated data are not needed.**

**A simplified cryogenic preconcentration, direct flame ionization (PDFID) method that is sensitive and provides accurate measurements of ambient NMOC concentrations has been developed and standardized sufficiently to be recommended for use by state and local air pollution control agencies in the development of their ozone control plans. Recent refinements to the method are discussed, an automatic remote sampling system is described, and the performance (precision and accuracy) of the method is characterized, based on results from utilization of the method for NMOC analysis of 1375 air samples collected from 22 sites during the summer of 1984.**

***This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

Accurate measurements of ambient concentrations of nonmethane organic compounds (NMOC) are important to the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants. Achieving and maintaining compliance with the National Ambient Air Quality Standards for ozone thus depends largely on control of ambient levels of NMOC.

A number of photochemical dispersion models have been developed to describe the quantitative relationships between ambient concentrations of NMOC and other compounds (e.g., $NO_x$) and subsequent downwind concentrations of ozone. An important application of such models is to determine the degree of control of NMOC that is necessary, in a particular area, to achieve compliance with applicable ambient air quality standards for ozone. To achieve this purpose, the models require input of accurate data on ambient concentrations of NMOC.

The more elaborate theoretical models generally require detailed organic species data. Such data must be obtained by analysis of air samples with a sophisticated, multicomponent gas chromatographic (GC) species analysis system. Simpler empirical models such as the Empirical Kinetic Modeling Approach (EKMA) require only total NMOC concentration data—specifically, the average total NMOC concentrations from 6:00 AM to 9:00 AM.

Until recently, ambient NMOC measurements for EKMA were often obtained with commercial, continuous NMOC

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analyzers. However, measurements from these instruments have been shown to be unreliable, particularly at concentrations below about 0.5 ppmC, due to a variety of instrument-related problems. These problems included (1) the indirect, subtractive nature of the measurement process employed (total organic compounds minus methane), (2) non-uniform per-carbon response for different compounds due to oxygen interference, (3) inadequate sensitivity, and (4) interference from water vapor. Thus, the usefulness of NMOC measurements obtained with these instruments is limited.

The GC speciation method provides more accurate and reliable ambient measurements. Utilizing cryogenic preconcentration followed by GC separation and flame ionization detection (FID), the technique provides quantitative, identified, species concentrations of the $C_2$ to $C_{10}$ compounds typically observed in ambient air. NMOC measurements may be obtained by summing the individual species concentrations. The cryogenic sample preconcentration greatly enhances the sensitivity of the method while effectively minimizing interference from methane and oxygen, allowing direct measurement of various organic species with little variation in the per-carbon response for most compounds of interest. However, the GC speciation method requires sophisticated analytical equipment, a high level of operator skill and experience, and considerable time per analysis, making such measurements expensive. This expense is often not justified in EKMA applications where speciated data are not required.

A number of researchers have contributed to the development of a simplified NMOC method—derived from the speciation method—that eliminates the GC separation and much of the operator skill required but retains the cryogenic preconcentration for good sensitivity, the FID for selectivity, and the inert carrier gas for uniform per-carbon response. This method has been further refined, tested, and sufficiently standardized to be an available and recommended method for the measurement of ambient concentrations of NMOC for EKMA or other applications. The method is identified as the preconcentration, direct flame ionization detection (PDFID) method for NMOC.

## Method Description

Figure 1 shows a schematic diagram of the basic analytical apparatus. Major components include a sample volume metering system, a six-port gas valve, a cryogenic preconcentration trap, and a FID-integrator-recorder system.

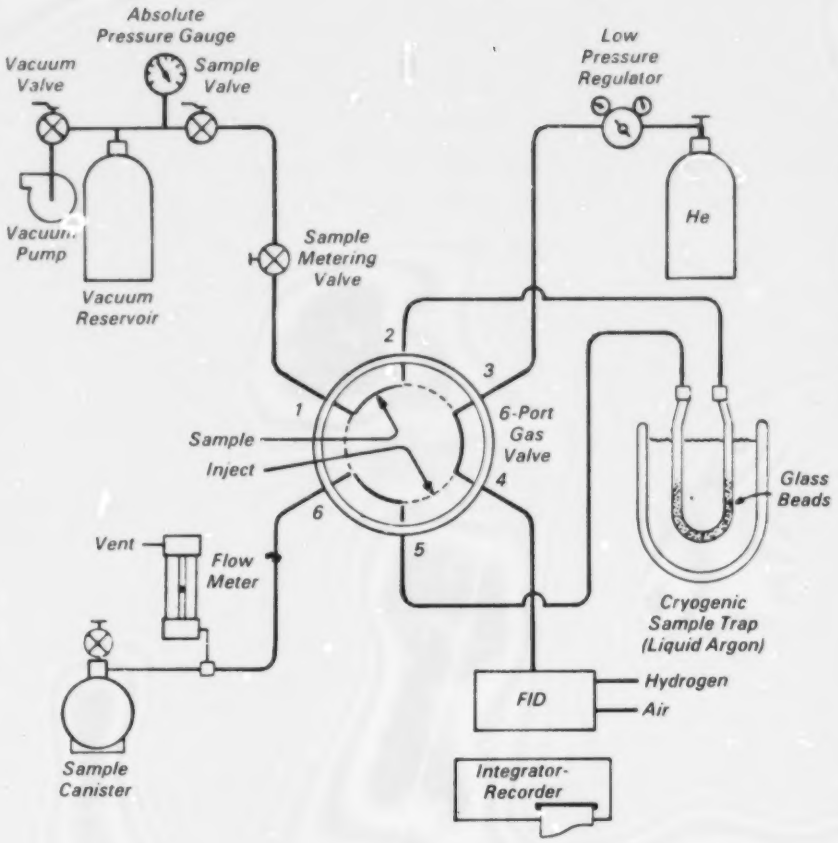


*Figure 1. Schematic diagram of system for analysis of total non-methane hydrocarbons by cryogenic preconcentration and flame ionization detection.*

The vacuum pump is used first to reduce the pressure in the vacuum reservoir to a known selected absolute pressure setting. With the gas valve in the sample (trapping) position, sample air is drawn through the trap, which is immersed in liquid argon (-186°C). The volume of air passing through the trap is measured by the increasing pressure (diminishing vacuum) in the reservoir, and the sample flow is stopped at a second selected pressure. The trap condenses NMOC while permitting air and methane to pass through. During the trapping mode, helium carrier gas passes through the gas valve directly to the FID.

Following the trapping mode, the gas valve is switched to the inject position, directing the helium carrier gas through the trap, in the direction opposite to the previous sample flow, before passing to the FID. The cryogen is then removed, and the trap is heated to approximately 90°C. Organic compounds collected in the trap revolatilize and are swept into the FID by the carrier gas. The resulting peaks are integrated and converted to ppmC by an NMOC calibration curve, prepared previously by using propane-in-air concentration standards. Use of the same precise reservoir pressure readings for each trapping cycle results in a constant sample volume and allows calibration of the system with known concentration standards without quantitatively measuring the actual sample volume.

A detailed description of the PDFID method, incorporating changes and refinements developed to date, is provided in an appendix to the full report.



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## Refinements

*Apparatus.* Various types of component flame ionization detectors, integrators, and chart recorders could be used to assemble the requisite analytical apparatus. However, a recent-model laboratory gas chromatograph provides the most advantageous and expedient way to obtain the necessary functions, even though no GC column is used. Such an instrument contains a high quality temperature-controlled FID, precision gas flow controls, and a properly interfaced signal integrator/recorder in a conveniently integrated system. Further, a chromatograph instrument also provides a temperature-programmable oven for warming the trap, and capability for controlling the valve operation and other procedural sequences. In addition, it provides a convenient mechanical facility for properly mounting the trap, valve, and other components so as to minimize the lengths of interconnecting lines and keep them heated above ambient temperature. These advantages help to minimize variability in the analytical measurements.

*Trap.* Use of a small, U-shaped trap packed with 60/80 mesh glass beads (as opposed to a multi-turn unpacked trap) provided better uniformity of per-carbon response to various paraffinic and olefinic hydrocarbon compounds and also more repeatably shaped peaks.

*Water Interference.* Some positive interference from moisture in the sample air was observed, manifested as a relatively uniform and predictable shift in the FID baseline during sample injection. This effect can be minimized to a large extent by (1) carefully observing the character of the baseline shift using humidified zero air and an expanded recorder scale, (2) adjusting the trap heating rate for uniform shift, and (3) programming the integrator to correct or compensate for the shift.

*Remote Sampling.* Collection of air samples at remote sites provides a number of advantages, including (1) collecting integrated (e.g., 3-hour) samples, (2) shipping and storing samples for convenient central laboratory analysis, (3) analyzing samples from several sites with a single analytical system, and (4) capability for repeat analysis of samples or collection of duplicate samples for quality assurance. NMOC samples have shown to be stable for several weeks when collected and stored in stainless steel canisters whose surface has been specially treated by the SUMMA process (Molectrics, Carson, CA). A sampling system, consisting of a metal bellows pump, hypodermic needle, filter, timer, and special electric solenoid valve, allows for automatic unattended collection at remote sites of 3-hour integrated ambient air samples in canisters. Such a system has been successfully demonstrated in a 22-site network operated for 12 weeks during 1984. Following analysis, the treated stainless steel canisters can be readily and easily cleaned and evacuated for reuse.

## Method Performance and Test Results

A 22-site, 12-week NMOC monitoring project during the summer of 1984 provided PDFID method performance data under actual field-use conditions. Three-hour air samples were collected in treated stainless steel canisters and shipped to a central laboratory for analysis using the PDFID analytical system. In all, 1375 valid samples were collected, ranging in concentration from 0.06 ppmC to 4.75 ppmC.

*Overall completeness* (number of valid samples obtained divided by the number expected) for the 22 sites, located in the eastern and central areas of the country, was 90.6 percent.

*Calibration drift* was observed with daily calibrations at the beginning of each day and calibration checks at the end of the day. Daily zero and span drifts are shown in Table 1.

*Analytical precision* for the method was assessed from the differences observed between the original analyses and later repeat analyses for 28 of the samples. The results are shown in Table 2. Since the mean difference is considerably smaller than the standard deviation, it can be concluded that the mean is not significantly different than zero, suggesting that the time delay between the first and second analyses had no significant effect on the concentration measurement.

*Overall precision* was assessed from the differences between the analyses of 58 pairs of duplicate samples collected simultaneously in duplicate, paired canisters. Accordingly, this overall precision assessment includes both analytical variability and variability contributed by collection and storage of the air samples in the canisters. The results are shown in Table 2. The overall precision is only slightly worse than the analytical precision, indicating that collecting and storing the air samples in the canisters added relatively little to the overall variability.

*Accuracy* is undefined because the NMOC measurements encompass an unspecified mixture of various organic compounds. Accuracy relative to internal propane standards was assessed with audit samples, prepared by diluting NBS-traceable propane standards with zero air into clean canisters at a pressure similar to the pressure used for ambient samples. The overall regression slope and intercept for 73 audit samples were 1.0296 ± 0.0154 and 0.0210 ± 0.0277 (95% confidence interval), respectively, indicating about a 3% positive bias and a small fixed offset.

Accuracy relative to GC speciation analysis was assessed by comparing the results from 336 samples that were independently reanalyzed by GC speciation (sum of species) analysis. A linear, orthogonal regression of these data is illustrated in Figure 2. The resulting slope of 1.081 and intercept of 0.015 indicated a modest bias of approximately +8% for the PDFID method compared to GC speciation analysis.

Accuracy relative to an independently operated PDFID analysis system was assessed by comparing the results from 120 samples that were reanalyzed by the independent system. An orthogonal linear regression resulted in a slope of 1.032

*Table 1. Daily Calibration Drift*

| | Zero Drift ppmC | Span Drift % |
|---|---|---|
| Maximum | +0.013 | 14.1 |
| Minimum | -0.016 | -10.1 |
| Mean | +0.00016 | + 1.47 |
| Standard deviation | 0.0022 | 4.06 |

*Table 2. Precision*

| | Analytical Precision | Overall Precision |
|---|---|---|
| Number of differences | 28 | 58 |
| Range of differences | -0.14 to +0.27 ppmC | -0.41 to +0.22 ppmC |
| Mean difference | +0.025 ppmC | -0.026 ppmC |
| Std. deviation of differences | 0.107 ppmC | 0.119 ppmC |
| Range of percent differences | -38.3% to +30.7% | -67.8% to 47.8% |
| Mean percent difference | 0.2% | -3.1% |
| Std deviation of % differences | 12.7% | 17.4% |



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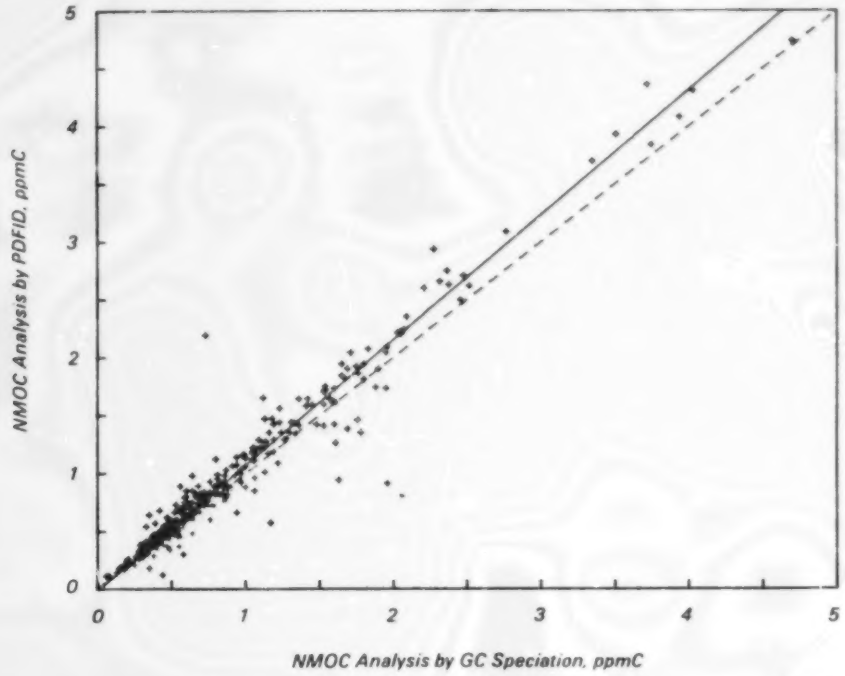


***Figure 2.*** *Comparison of PDFID measurements to GC speciation measurements for 336 ambient samples.*

and an intercept of -0.1891, showing generally good agreement between the two independently operated PDFID analytical systems.

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*The complete report, entitled "A Cryogenic Preconcentration—Direct FID (PDFID) Method for Measurement of NMOC in Ambient Air," (Order No. PB 86-120 631/AS; Cost: $11.95, subject to change) will be available only from:*

*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*

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